



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Michael D. Gilbert Art Unit : 1771
Serial No. : 09/352,976 Examiner : Victor S. Chang
Filed : July 14, 1999
Title : ELECTRICALLY DISBONDING MATERIALS

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF A.C. MAKRIDES UNDER 37 C.F.R. § 1.132

I, Alkis C. Makrides, declare as follows:

1. I am a citizen of the United States and currently live at 50 Grafton Street, Newton, MA 02459.
2. I received a Bachelor's degree in Chemistry from the University of Texas (Austin) in 1951 and a Ph.D. in Physical Chemistry from the University of Texas (Austin) in 1957.
3. I was employed by Union Carbide Metals Company (Niagara Falls) as Research Chemist from 1957-1959; by Mobil Oil Company (Dallas) as Senior Research Chemist from 1960 to 1962; by Tyco Laboratories, Inc. (now Tyco International) as Group Leader, Associate Director of Research, Director of Research, and Vice President from 1962 to 1970; by EIC Laboratories, Inc. as President and Chief Executive Officer from 1971 to present.
4. I have conducted research in Electrochemistry, Batteries, Surface Chemistry (Adsorption and Catalysis), and Corrosion for over twenty years.
5. I have been employed by EIC Laboratories, Inc. since 1971, and my current position is Chief Executive Officer and my responsibilities include the overall direction of the research work at EIC Laboratories.
6. A list of my articles, patents, and patent applications is attached.

7. I have examined and reviewed Moulton et al., U.S. Patent No. 5,441,830 ("Moulton"), and Koga et al., U.S. Patent No. 5,565,284 ("Koga") in detail. I have also examined and reviewed the Office Action dated 03/22/2005.

8. A fundamental fact of all electrochemical systems is that the interface between two electronically conducting phases cannot support an electrochemical (or faradaic) reaction. This fundamental fact is reflected in the requirement that an ionic electrolyte is a necessary component of all electrochemical devices (batteries, fuel cells, etc.). A potential gradient between electronic conductors causes a flow of electrical (electronic) current; a voltage gradient between an electronic conductor and an ionic conductor may cause a chemical reaction.

9. The assertion that Moulton's composite electrode discloses on the claimed invention is flawed because Moulton's composite electrode – or any other composite or solid electrode – is by necessity an electronic conductor. If it is not, then it is not a useful "electrode." As an electronic conductor, it cannot support a faradaic reaction at the electrode/current collector interface. In fact, if such a reaction were possible, the device incorporating such an electrode would fail, probably catastrophically.

10. The Examiner notes that "Moulton's teaching of methods for enhancing the adhesion of composite electrodes onto conductive foils implicitly teaches that while the bond can be enhanced, eventually it can be disbonded, i.e. disbondable". This argument is not germane to the claimed invention. Any bond can eventually be disbonded in some fashion – for example, by applying sufficient force on the interface. The invention claims an easy, quick, and reliable method, namely the application of a voltage to produce a faradaic reaction at the interface.

Moulton is actually explicit about the modes of disbonding. To quote "when conductive plastic foils are used as the current collector, they are in direct contact with a composite electrode and are susceptible (sic) to swelling due to contact of the current collector with the electrolytic solvent found in the electrode. Such swelling adversely affects the performance of the battery" (Col. 1, lines 50-57). Also, Moulton notes that bonding of a composite electrode to the current

collector may be poor in the first place and notes that "the paste can become dislodged from the foil. In turn, such dislodgement will result in defects in collecting current from that cell" (Col. 1, lines 67-68, Col. 2, lines 1-2). Neither "disbonding" mechanism involves the application of voltage across the interface or a faradaic reaction at the interface.

11. The Examiner notes "that it is old and well known that the bond between a composite electrode and an electrically conductive surface is weakened by a faradaic reaction at the interface, as evidenced by the teaching of Koga which expressly teaches that charge-discharge cycles exacerbates (sic) the interfacial adhesion (bond) between the current collector and the electrode layer (Col. 1, lines 39-52)."

This statement confuses interfaces – Koga does not refer to the interface between "a composite electrode and an electrically conductive surface" or to a faradaic reaction at this interface, which, as we pointed out before, is not possible. Actually, Koga is describing a bulk effect, the expansion and contraction of lithiated and delithiated electrode material which leads to fracture of the material and shedding of "fine particles". As he points out, this is a result of "numerous repetition of charge-discharge cycles" (Col. 1, line 42) and is unrelated to the disbonding described in the present invention which occurs after a single, short application of a voltage across the bond interface.

12. There are a number of other confused statements by Moulton and, derivatively, by the Examiner. For example, Moulton claims in his definition of composite electrodes the inclusion of "an alkali salt" (Col. 8, line 16). This is in fact incorrect – the salt must be a lithium salt; other alkali salts will not do since batteries utilizing alkali metals other than lithium are unknown. On his part, the Examiner notes that V_6O_{13} is "prepared by heating ammonium metavanadate ($NH_4^+VO_3^-$), i.e. an ammonium salt (Col. 18, lines 57-61)." Of course, the purpose of the heating is to drive off ammonia so that the final composition contains no ammonium salt – contrary to the present invention which uses an ammonium salt.

What is crucial is the fundamental difference between, on the one hand, a composite electrode – a structure composed up to 90% of some electrochemically active compound, usually an oxide, which is either intrinsically electronically conductive or can be made so by the addition

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of an electronic conductor, usually carbon, held together by a binder and, on the other hand, an adhesive containing an electrolyte which supports an electrochemical (faradaic) reaction at the bonding interface. These two materials are fundamentally different, notwithstanding the inclusion, in varying amounts, of some common ingredients. In short, a composite electrode is not an electrochemically disbondable adhesive, even with the inclusion of binders for holding together its components, since an electrode is necessarily an electronic conductor.

13. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the instant patent application or any patent issuing thereon.

Dated: 6-22-2005

Alkis C. Makrides
Alkis C. Makrides



A.C. MAKRIDES
CEO
EIC LABORATORIES, INC.

Education:

Ph.D., (Physical Chemistry), University of Texas, 1957.
B.A. (Summa Cum Laude), University of Texas, 1951.
Research Fellow, Institute for the Study of Metals, University of Chicago, 1954-55.
Research Fellow, American Petroleum Institute, University of Texas, 1955-57.

Professional Experience:

1971 - Present	President and CEO, EIC Laboratories, Inc.
1970 - 1975	Adjunct Professor of Chemistry, Boston College, Boston, MA. Associate Director, Environmental Center, Boston College, Boston, MA.
1962 - 1970	Director of Research, Vice President, Tyco Laboratories, Inc., (Now Tyco International), Waltham, MA.
1960 - 1962	Senior Research Chemist, Mobil Oil Company, Dallas, TX.
1957 - 1959	Research Chemist, Union Carbide Metals Company, Niagara Falls, NY.

Professional Societies:

Member of the American Chemical Society, The Electrochemical Society, Faraday Society, American Institute of Chemists, New York Academy of Sciences, National Association of Corrosion Engineers.

Honors:

Scholastic:	Phi Beta Kappa, Tau Beta Pi, Phi Lambda Upsilon, Omega Chi Epsilon, Phi Eta Sigma, Sigma Xi.
Professional:	Turner Memorial Award of the Electrochemical Society, 1957. Young Author's Prize of The Electrochemical Society, 1960.

Accomplishments:

Dr. Makrides has carried out and directed research and development in adsorption, catalysis, chemical kinetics, electrochemical kinetics, thermochemistry, batteries, and corrosion. Dr. Makrides is the author of numerous reports on government sponsored research and development, and a number of patents.

Publications:

Adsorption and Catalysis:

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Removing Carbon Oxysulfide from Gas Streams, November 1981, US 4,298,584 and corresponding foreign patents.

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SECOND EDITION

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John S. Newman

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Introduction

1

Since the fundamental aspects of electrochemistry are to be developed, in order, in Parts A, B, and C, this chapter has been designed to introduce important concepts related to the flow of fluids, mass transfer, interfacial phenomena, and electrochemical thermodynamics. For accomplishing this purpose, it seems appropriate to begin with a superficial consideration of the behavior of a particular electrochemical system. In this way the reader can see how these factors act, and interact with each other, to determine system behavior. He can then proceed with an overall view of the ultimate utility and application of the detailed material as it is presented subsequently. Since essentially all the material in Chapter 1 will be repeated later with a more thorough development, reference to original work and collateral reading will be postponed.

1.1 THERMODYNAMICS, ELECTRODE KINETICS, AND TRANSPORT PROCESSES

The analysis of electrochemical systems draws primarily on three fundamental areas of electrochemistry.

Thermodynamics provides the framework for describing the properties of electrolytic solutions and their dependence on composition, temperature, and pressure. This is a macroscopic science and hence provides an appropriate basis for our studies, since the system behavior need not be correlated with microscopic or molecular concepts. Thermodynamics also provides a

framework for describing reaction equilibria and thermal effects, which manifest themselves most directly in equilibrium cell potentials. Furthermore, the driving forces for irreversible processes are conveniently expressed in thermodynamic terms.

Departures from equilibrium conditions are inherent in the application of electrochemical systems. *Electrode kinetics* concerns the nonequilibrium driving force, or *surface overpotential*, necessary to make heterogeneous electrode reactions proceed at appreciable rates. Here again, we seek to express relationships among macroscopically measurable quantities as they will affect system behavior.

Of equal importance are irreversibilities associated with *transport* in electrolytic solutions. These are responsible for ohmic losses and heating in the solutions, and for limited rates of transfer of reactants to electrodes and products away from electrodes.

1.2 ROTATING CYLINDERS

To illustrate the applications of these fundamental areas of thermodynamics, electrode kinetics, and transport phenomena, Chapter 1 will consider their use in the analysis of a simple electrochemical system; namely, two concentric, cylindrical electrodes with an electrolytic solution in the annulus between the two, as shown in Figure 1.1. The application of an

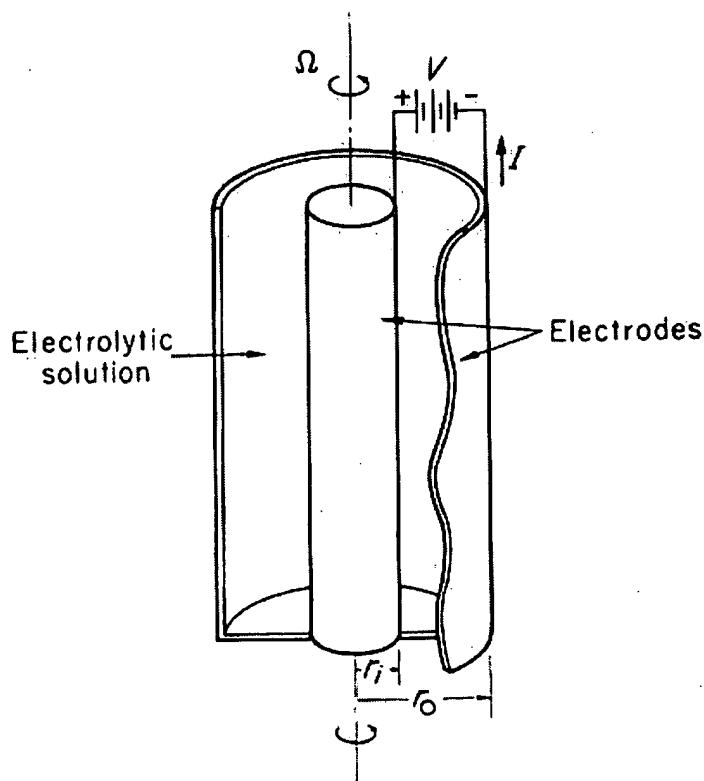


Figure 1.1 System of cylindrical electrodes, the inner of which can rotate.

responds to subtracting the ohmic contribution that would exist in the absence of concentration variations. This definition of concentration overpotential differs from the preceding one by the integral in equation 1.24, which is the difference in the ohmic contribution with and without concentration variations. This term can thus be logically associated with concentration variations near electrodes.

In the present case, with the conductivity related to the concentration by equation 1.6 and with an assumed linear variation of concentration in the diffusion layer, the concentration overpotential can be expressed as

$$\eta_c = \frac{RT}{F} \left[\ln \frac{c_0}{c_b} + t_+ \left(1 - \frac{c_0}{c_b} \right) \right], \quad (1.25)$$

where c_0 refers to the concentration immediately adjacent to the surface of the working electrode.

One of the advantages of this modified definition of the concentration overpotential stems from the fact that the potential difference $\Phi_1 - \Phi_2$ can now be expressed as

$$\Phi_1 - \Phi_2 = \Delta\Phi_{\text{ohm}} + \eta_c(\text{anode}) - \eta_c(\text{cathode}), \quad (1.26)$$

where in this case $\Delta\Phi_{\text{ohm}}$ can be calculated without regard for the concentration variations near electrodes and is, in fact, given by equation 1.10. The difference between these two definitions is probably not important except for solutions of a single electrolyte, such as the cupric sulfate solutions being considered here. In detailed calculations for many electrochemical systems, it is desirable to calculate the potential distribution in the bulk solution somewhat separated from the details of the calculations of concentration variations near electrodes. The principal disadvantage of the second decomposition of potentials lies in the fact that it is different from the decomposition of potential differences by interrupter methods.

Figure 1.9 shows the concentration overpotential at a cathode for currents up to the limiting current.

1.8 SURFACE OVERPOTENTIAL

An additional contribution to the overall cell potential is the driving force required to make the electrode reactions proceed at appreciable rates. The *surface overpotential* is defined as the potential of the working electrode relative to a reference electrode of the same kind placed in the solution adjacent to the surface of the working electrode. This reference electrode is thus one of those used to define the concentration overpotential. For example, at the anode in Figure 1.8, the surface overpotential is

$$\eta_s = \Phi(\text{anode}) - \Phi_1. \quad (1.27)$$

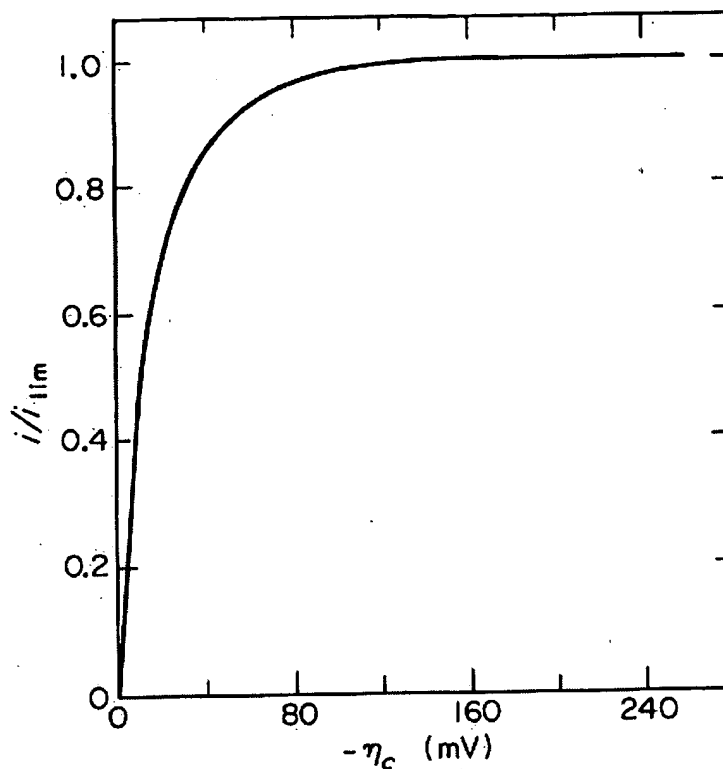


Figure 1.9 Concentration overpotentials at a cathode in 0.1 M CuSO_4 .

The rate of the electrode reactions is the rate of dissolution or deposition of copper, and this can be conveniently measured by the current density at the electrode. By convention, the current density is positive when it flows from the electrode into the solution. Thus, current densities are positive at anodes and negative at cathodes.

The current density depends on the driving force and thus is related to the surface overpotential and the composition of the solution at the interface, as well as the temperature. For example, the current density can frequently be expressed as

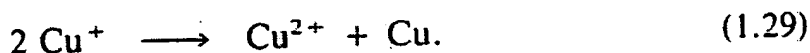
$$i = i_0 \left[\exp \left(\frac{\alpha_a F}{RT} \eta_s \right) - \exp \left(- \frac{\alpha_c F}{RT} \eta_s \right) \right]. \quad (1.28)$$

This is similar to the expression of the rate of a nonelectrochemical, heterogeneous reaction. The first exponential term can be regarded as representing the rate of the anodic process, and the second term, that of the cathodic process. These are governed by activation energies which depend on the surface overpotential.

When $\eta_s = 0$, the anodic and cathodic currents are equal in magnitude to each other and to i_0 . This is an important kinetic parameter and is termed the *exchange current density*. Different reactions may have exchange current densities that differ by many orders of magnitude. Furthermore, the exchange current density depends strongly on the composition at the interface

and on the temperature. α_a and α_c are two additional kinetic parameters and may be termed *apparent transfer coefficients*. They usually have values between 0.2 and 2.

Equation 1.28 serves to show explicitly a typical dependence of reaction rate on surface overpotential. The dependence on composition and temperature is not shown explicitly, since i_0 depends on these factors in an unspecified manner. Many reactions, such as those involving oxide formation, are complicated and do not follow equation 1.28. Even the relatively simple copper electrode is complicated. At high anodic rates, appreciable amounts of cuprous ions are formed. These subsequently disproportionate in the solution to yield cupric ions and copper, which precipitates,



It should also be noted that the value of i_0 can depend on the composition and preparation of the electrode and on the presence of impurities.

With these words of caution, we introduce equation 1.28 to describe electrochemical kinetics in general or in the absence of detailed information. It should be emphasized that the goal here is to relate the reaction rate or current density to conditions prevailing at the interface itself. Thus, we define the surface overpotential in terms of a reference electrode well within the diffusion layer, adjacent to the electrode surface; and we seek to relate the kinetic parameters to the composition adjacent to the electrode, not to the composition of the bulk solution or to concentration gradients near the surface.

The exchange current density is a measure of the freedom from kinetic limitations. A reaction with a large value of i_0 is frequently said to be *fast* or *reversible*. For large values of i_0 , a given current density can be obtained with small surface overpotentials.

Figures 1.10 and 1.11 illustrate the behavior of equation 1.28. One can see that higher values of i_0 give higher values of the current density at a given surface overpotential. Figure 1.11 is a so-called Tafel plot, used because, at high surface overpotentials, one of the terms in equation 1.28 becomes negligible, and a straight line is obtained on a semilogarithmic plot. Thus

$$i = i_0 \exp \left(\frac{\alpha_a F}{RT} \eta_s \right) \quad \text{or} \quad \eta_s = 2.303 \frac{RT}{\alpha_a F} \log \frac{i}{i_0} \quad (1.30)$$

for $\alpha_a F \eta_s \gg RT$;

$$i = -i_0 \exp \left(-\frac{\alpha_c F}{RT} \eta_s \right) \quad \text{or} \quad \eta_s = -2.303 \frac{RT}{\alpha_c F} \log \left| \frac{i}{i_0} \right| \quad (1.31)$$

for $\alpha_c F \eta_s \ll -RT$.

The *Tafel slope*, either $2.303 RT/\alpha_a F$ or $2.303 RT/\alpha_c F$, is thus seen to be inversely proportional to the apparent transfer coefficients.